

PHOTOCHEMICAL REDUCTION OF THIONINE BY N-PHENYL GLYCINE IN METHANOL

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الخلاصة :

تستقصي هذه الدراسة اختزال الثيونين الضوئي بواسطة (ن-فينيل جلسرين) N-phenylglycine في وسط ميثانولي مطلق . ولتحقيق ذلك قُمنّا بتركيب جهاز لتشعيع المحلول بضوء أحادي التردد ذي شدة إضاءة معلومة . وجدنا أن الكفاءة الكمية (Φ) للضوء الأصفر لتَحُلُّل الثيونين تعتمد على تركيز المادة المُختَزَلَة ، ودرجة الحموضة ، ودرجة الحرارة . غير أنها لا تعتمد على تركيز مادة الثيونين .

ثم قمنّا بتحليل هذه النتائج بافتراض ميكانيكية للتفاعل ، حيث عملنا على حساب ثوابت نسبة معدلات التفاعل . ووجدنا أن الكفاءة الكمية تُحدد من خلال الإتران بين :

- ١ - الحالة الثلاثية البروتونية للثيونين مع البروتون والحالة الثلاثية البروتونية للثيونين .
- ٢ - الحالة الثلاثية البروتونية للثيانين مع المادة المُختَزَلَة مع المركبات المعقدة الناتجة عن تفاعل الثيونين والمادة المختزلة .

ABSTRACT

The photochemical reduction of thionine by *N*-phenylglycine in absolute methanol was investigated. An apparatus for the irradiation of an air-free solution with known intensities of monochromatic light was constructed. The quantum efficiency, in yellow light, for the disappearance of thionine, was found to be a function of reductant concentration, acidity, and temperature. The quantum efficiency (ϕ) was found to be independent of the concentration of thionine.

The results have been interpreted in terms of a reaction mechanism. Ratios of the relevant rate constants for the proposed mechanism have been evaluated. It was found that the quantum efficiency is controlled by two equilibria between (i) the triplet state of thionine with proton, and the protonated triplet state of thionine; and (ii) the protonated triplet state of thionine with reductant, and associated complex of thionine with reductant.

PHOTOCHEMICAL REDUCTION OF THIONINE BY *N*-PHENYLGLYCINE IN METHANOL

INTRODUCTION

Dubien *et al.* [1] studied the photoreduction of thionine with dia-Na EDTA and nitriloacetic acid (NTA). Faure *et al.* [2-4] established that the primary photochemical act in the case of thionine is electron abstraction by the protonated triplet dye. Koizume *et al.* [5] found that photoreduction to the leuco form without the reducing agent does not occur in indo-phenol and phenazine dyes but is apparently specific for thiazine dyes as such methylene blue, methyl green, toluidine blue, and thionine. Photoreduction of methylene blue and thionine in ethanol was studied by Usui [6]. It was found that as the initial dye concentration was varied in the region $10^{-6} - 10^{-5}$ mol dm⁻³ for both methylene blue and thionine, the overall second order rate constants (k), decreased. Photoreduction of thionine and methylene blue in aqueous solutions were studied by several workers [6-14]. In aqueous solutions, (i) pulse radiolysis of thionine and methylene blue and (ii) formation of e_{aq}^- from excited thionine and methylene blue were also studied by Solar *et al.* [15] and Vonnach *et al.* [16]. Guler *et al.* [17] studied the photoreduction of methylene blue and thionine by water.

The present paper summarizes the studies of the effect of acidity, and concentration of phenylglycine, concentration of thionine on the quantum efficiency of the photochemical reduction of thionine, using methanol as nonaqueous medium.

EXPERIMENTAL

E. Merck oxidation-reduction indicator, thionine, was used. Acridine, as fluorescent indicator, from B.D.H. was used. All other chemicals used were of E. Merck. Nitrogen gas was supplied by Pakistan Oxygen Ltd. (99.98%). Traces of oxygen were also removed from nitrogen by a method described by Fieser [18]. The stock solutions of thionine were preserved in well-stoppered polythene bottles, as suggested by Sawkar [19].

An apparatus for irradiation of deoxygenated reaction solutions with monochromatic light was designed as shown in Figure 1. The 250 watts high pressure mercury ME/D compact source Mazda box type G.E.C. lamp (Code No. 2191-0521) was run on 220 volts AC mains using the circuit shown in Figure 1. The light from the arc was focused by a combination of two convex lenses L_1 and L_2 onto a small hole (O) 2 mm, in a metal plate. This helps to cut off the stray light; only light from the centers of the arc is used. L_3 represents a lens which was placed at its focal length from the hole in the metal plate, O, to obtain a parallel beam of light. Monochromatic yellow light was obtained by passing the beam through a further combination of filter solutions held in two compartments cells (F_1 and F_2). To isolate the 579 nm light, the filter solutions [20] in F_1 and F_2 were used. The combination consisted of 10 ml $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 100 gm in 1 liter water) + 90 ml (333 gm anhydrous CaCl_2 in 1 liter H_2O *i.e.* 3.0 mol dm⁻³), 1 cm, in the first compartment (F_1) and standard potassium dichromate solution, 1 cm, in the second compartment of the filter cell (F_2). R denotes the plain reflecting glass which reflected about 10.5% of the filtered light on to a photocell P_2 . The light was then passed through the reaction cell (C). M is a magnetic stirrer. P_1 and P_2 represent the photocells used to follow the reaction and to monitor the light beam, respectively. G_1 and G_2 refer to the galvanometers used to indicate the responses of the photocells P_1 and P_2 , respectively.

The doubled-walled reaction cell, as shown in Figure 2, was a modified form of the cell used by Atkins [21], Sawkar [19], and Ahmed [22]. It was a cylindrical glass tube, 7.0 cm in length, 2.5 cm in diameter with flanged

ends. At the ends of the reaction cell, two joints W (as shown in Figure 2) were connected to a thermostatic bath (type T 52, manufactured by Haake, Karlsruhe/Germany) for circulation of water in the outer part of the cell. Circulation of water maintained the temperature of the reaction cell constant. The solution in the reaction vessel was magnetically stirred with the aid of a small horseshoe magnet, shown in Figure 2, placed on an electric motor.

The intensity of light (I_0) was determined with a photoemission cell connected in series with an ammeter. The photoemission cell is a diode whose cathode is coated with potassium and caesium oxides. The current flowing after impinging of light is proportional to the amount of light striking the cathode. $I = kI_0$, where k is the constant and I_0 is the amount of light measured in lumen. This equation shows that the diode current is a function of amount of light. It is possible to calibrate an ammeter in terms of lumens, since one lumen = $1/680$ light watt = 0.00147 light watt. The energy of a photon is given by $E = Nh\nu = Nhc/\lambda$ where $N =$ Avogadro's number (6.023×10^{23}), $h =$ Planck's constant (6.62×10^{-27} ergs/s), $\lambda =$ wave length of light (579 nm for yellow light), $\nu =$ frequency of yellow light used, $c =$ velocity of light (2.998×10^{10} cm/s). Therefore, $E/s = 2.066 \times 10^5$ J/s, since 1 watt = 1 J/s. Again one Einstein per second (E/s) = 2.066×10^5 watt. It is obvious that $I_0 = I/k = x/k$ where $x = x_2 - x_1 = I$, where x_1 is the value of current recorded on the ammeter for the situation when there is no light striking the photocell, x_2 represents the value of current on the ammeter when the photocell is exposed to light, and x is the effective value of the current recorded on the

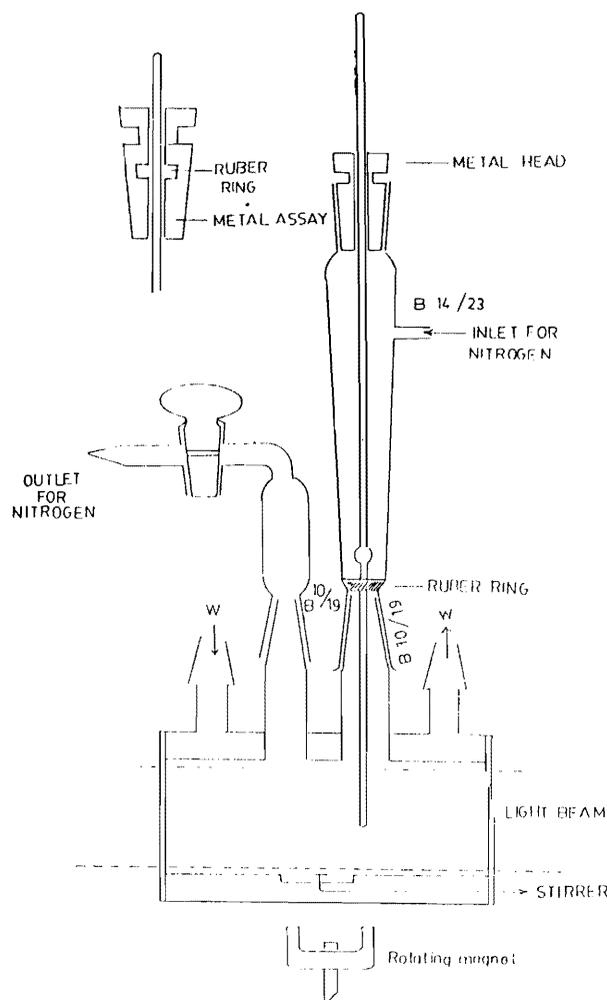


Figure 2. The Reaction Cell.

ammeter. As $1 \text{ E/s} = 2.066 \times 10^5 \text{ watt}$ and $k = 20$, *i.e.* the photocell constant, $(x/k) \times 0.00147 \text{ watt} = (x/20) \times 0.00147 \times (1/2.066 \times 10^5) \text{ E/s}$, therefore,

$$I_0 = \frac{x}{20} \times \frac{0.00147}{2.066 \times 10^5} \text{ E/s.} \quad (1)$$

In the present work [23] it was decided to use the basic indicator, acridine, and optical method for the determination of the acidity of the reaction solution. The acidity scale on which the measurement were expressed was based on the Hammett acidity function with alcoholic acridine solution as the standard. The acidity of the reaction solution was controlled by using buffer solutions (mixture of sodium acetate and hydrochloric acid solution). If the extinction of the indicator in extreme acidic and basic solutions are d_1 and d_2 , then for a solution of intermediate acidity, the extinction d could be expressed as:

$$H_0 = \text{p}K - \log \frac{(d_1 - d)}{(d - d_2)}. \quad (2)$$

For the present work Weller's value [24] of $\text{p}K$ for aqueous acridine solution was taken as 5.45.

The Mazda lamp was on for 30 minutes before exposing the reaction solution to monochromatic yellow light. The dry reaction cell containing the magnetic stirrer was placed in the cell holder. It was kept in the dark with the help of shutters. 32.5 ml of the reaction solution was prepared by pipetting known volumes of stock solutions of thionine, *N*-phenylglycine and the buffer solution into reaction vessel. The cell was filled with the nitrogen retractable bubbler and the outlet tap. The cell was also filled with the water inlet and outlet taps connected to the thermostatic bath. Purified nitrogen was bubbled through the corresponding solvent to saturate it with the vapors of the solvent. It was then bubbled through the reaction mixture. The solution was stirred simultaneously during the flushing and irradiation periods. After deoxygenation of the solution for about 40 minutes, the bubbler was retracted without admitting air into the reaction cell. Nitrogen was kept flowing over the surface of the reaction solution (or the flow of nitrogen was maintained during the run). The photocell responses were noted with no cell in the beam (D_0) and with the cell containing the solvent (D_m). The reaction was followed by noting the photocell responses corresponding to the absorption of the dye from the deflection on the scale on the galvanometer and then the change in the transmission after every 10 seconds (D_{nt}). Simultaneous readings were taken on the reference galvanometer. During the flushing period, the hydrogen ion activity (H_0) for the reaction mixture was measured.

RESULTS AND DISCUSSION

The quantum efficiency (ϕ) for the disappearance of thionine was calculated using the following expression:

$$\log \left(\frac{D_m - D_{nt}}{D_{nt}} \right) = \frac{I_0(1 - \alpha)\phi\varepsilon Lt}{v} + \log \left(\frac{D_m - D_{ni}}{D_{ni}} \right). \quad (3)$$

The plot of $\log [(D_m - D_{nt})/(D_{nt})]$ against time (t) should be a straight line. The slope of the straight line is:

$$\text{Slope} = \frac{I_0(1 - \alpha)\phi\varepsilon L}{V}. \quad (4)$$

ϵ , the molar extinction coefficient for thionine in absolute methanol at 605 nm, was observed as $8.46 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. L , the length of the path traveled by the beam in the cell, was 7.0 cm. V , the volume of the solution was taken as 0.0325 dm^3 . I_0 and α (the fraction of the light lost at each window) were measured during the experiments. Now,

$$\phi = 5.488 \times 10^{-8} \times \text{slope} / I_0(1 - \alpha) . \quad (5)$$

Solution of thionine and *N*-phenylglycine in absolute methanol were deoxygenated for fifty minutes by bubbling oxygen free nitrogen through the solutions. It is seen from Table 1 that the solutions should be deoxygenated for at least thirty minutes before irradiation. A plot of $\log [(D_m - D_{nt}) / D_{nt}]$ against time is shown in Figure 3. No detectable reaction takes place if the reaction solution are irradiated without deoxygenating the reaction solution.

The effect of the variation of *N*-phenylglycine concentration on the quantum efficiency was studied for two different H_0 values at the same value of thionine concentration. The results are shown in Table 2. It is clear from Table 2 that the quantum efficiency at a fixed H_0 increases with the rise in the concentration of *N*-phenylglycine. The plots of $1/\phi$ against $1/[\text{AH}_2]$ shown in Figure 4 are straight lines. The values of quantum efficiencies for infinite concentration of *N*-phenylglycine at H_0 5.57 and 5.90 are 0.336 and 0.625, respectively.

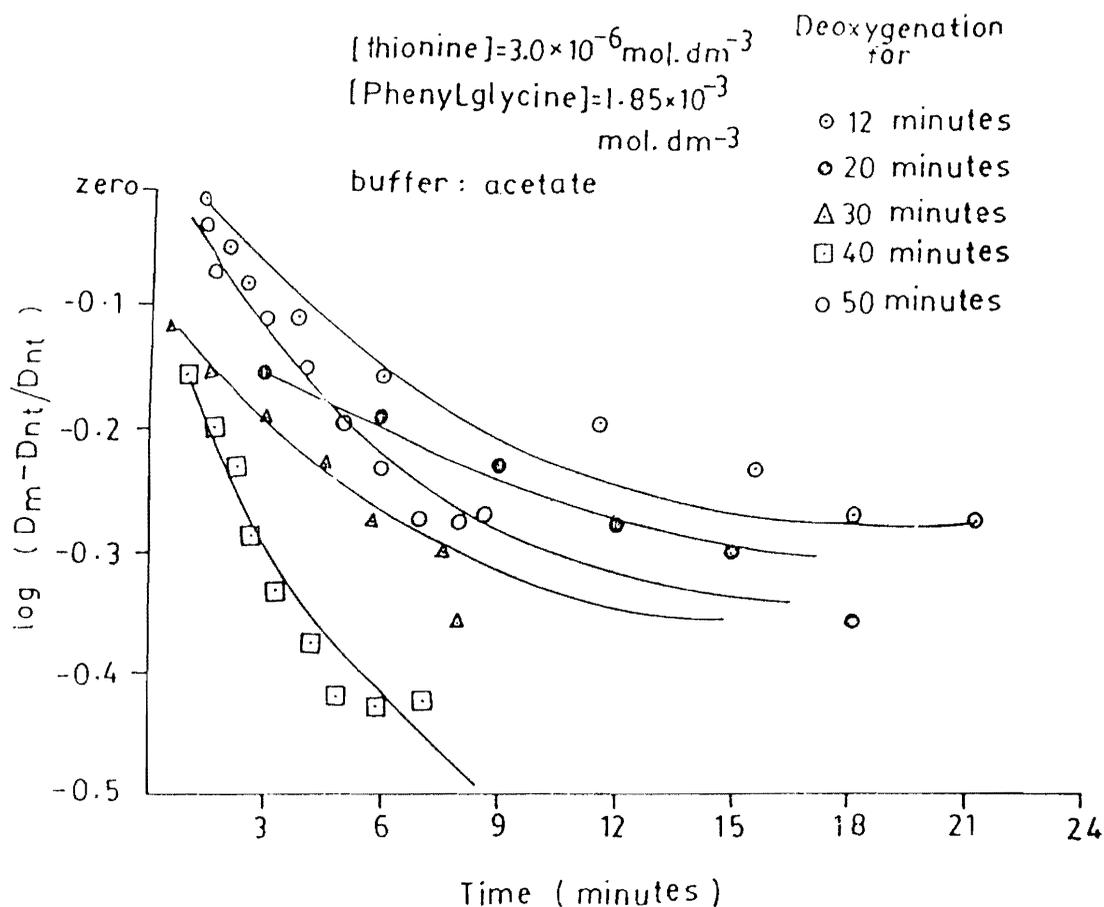


Figure 3. The Effect of Duration of Nitrogen Flow on the Quantum Efficiency of the Reaction Between Thionine with Phenylglycine in Absolute Methanol.

Table 1. Dependence of the Quantum Efficiency (ϕ) on the Duration of Nitrogen Flow.

Solvent: Absolute methanol			Buffer: Acetate	
10^6 [Th] (mol dm ⁻³)	10^3 (<i>N</i> -Phenylglycine) (mol dm ⁻³)	Nitrogen passed for time (minutes)	10ϕ	
3.0	1.85	12	0.53	
3.0	1.85	20	0.50	
3.0	1.85	30	1.56	
3.0	1.85	40	1.68	
3.0	1.85	50	1.67	

Table 2. Variation of *N*-Phenylglycine Concentration [AH₂] with Quantum Efficiency.

[Thionine] = 3.0×10^6 mol dm ⁻³			Buffer: Acetate	
Solvent: absolute methanol			Temperature: $25 \pm 0.1^\circ\text{C}$	
10^4 [AH ₂] (mol dm ⁻³)	$10^{10}I_0$ (E/s)	ϕ	$10^{-3}/[\text{AH}_2]$ (dm ³ /mol)	$1/\phi$
<i>H</i> ₀ (average): 5.57				
3.08	3.25	0.068	3.25	14.71
4.61	2.95	0.096	2.17	10.42
6.61	3.16	0.114	1.62	08.77
13.85	2.95	0.160	0.72	06.26
16.92	2.99	0.200	0.59	05.00
36.92	2.95	0.268	0.27	03.76
73.80	2.99	0.312	0.13	03.20
<i>H</i> ₀ (average): 5.90				
3.08	3.16	0.084	3.25	11.90
4.61	3.07	0.122	2.17	08.20
6.16	2.99	0.156	1.62	06.40
13.85	2.95	0.235	0.72	04.25
16.92	2.91	0.294	0.59	03.40
36.92	3.11	0.425	0.27	02.35
73.80	3.03	0.518	0.13	01.93

For the study of the effect of acidity on the quantum efficiency, measurements were carried out using *N*-phenylglycine in absolute methanol. The results are presented in Table 3. The plot of ϕ against H_0 is shown in Figure 5. It is evident that the quantum efficiency is found to decrease with a rise in the acidity. Taking ϕ_1 and ϕ_2 at the extreme values of low and high acidities as 0.350 and 0.038, respectively, $(\phi_1 - \phi) / (\phi - \phi_2)$ was plotted against $1/h_0$. The plot (Figure 6) is a straight line passing through the origin.

Thionine in various concentration and *N*-phenylglycine were irradiated in buffered methanol solutions. The results are presented in Table 4. Table 4 shows that the quantum efficiency is independent of the concentration of thionine, for a fixed value of concentration of the reductant at a fixed value of acidity. Matsumoto [25] also found that, the quantum efficiency is practically independent of the dye (methylene blue) concentration in the $(1 - 5) \times 10^{-6}$ mol dm⁻³ range at a fixed value of pH = 7.0, with *p*-chlorophenylglycine of concentration 1.0×10^{-4} mol dm⁻³. Ahmed [22] also reported that the quantum efficiency is independent of the concentration of thionine with allylthiourea and anethole in absolute methanol.

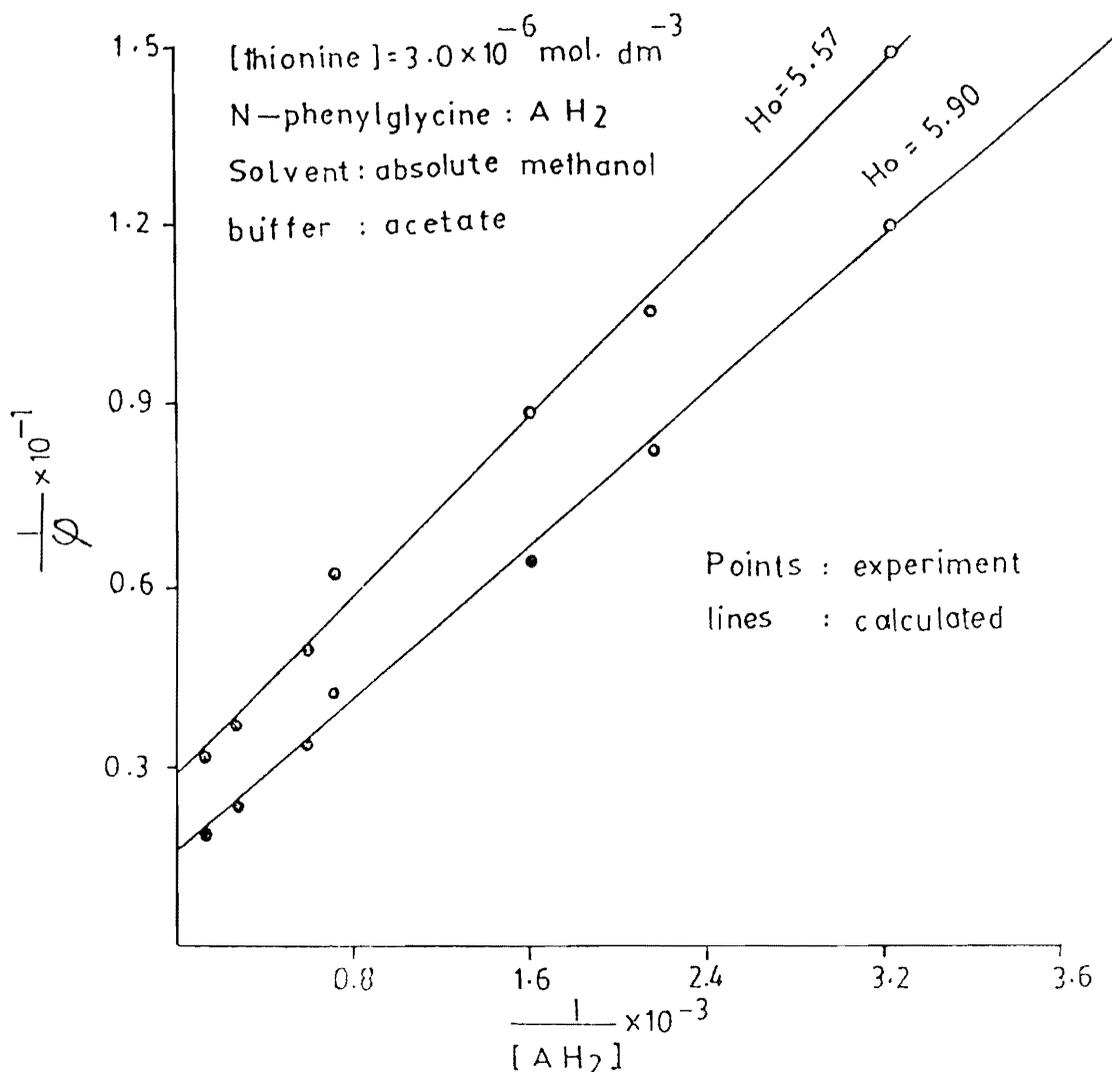


Figure 4. The Effect of Concentration of *N*-Phenylglycine on Quantum Efficiency.

The shape of the plot ϕ against H_0 shown in Figure 5 shows that the quantum efficiency may be controlled by two excited species of thionine. It is assumed that the triplet state must be initially formed as $^1\text{ThH}^+$. If the effect of acidity on the triplet state is the result of the competition between $^1\text{ThH}^+ + \text{H}^+ \rightarrow ^3\text{ThH}_2^{++}$ and $^1\text{ThH}^+ + \text{AH}_2 \rightarrow \text{products}$, an increase in acidity will cause a decrease in quantum efficiency. This is similar to the observed behavior. It is also assumed that $^3\text{ThH}_2^{++}$ associates with AH_2 and the following equilibrium is established:

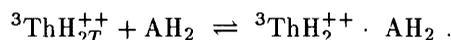


Table 3. Acidity-Quantum Efficiency for Thionine-Phenylglycine System.

[Thionine] = 3.0×10^6 mol dm ⁻³		Buffer: Acetate		
Solvent: absolute methanol		Temperature: $25 \pm 0.1^\circ\text{C}$		
H_0	$10^{10}I_0$ (E/s)	ϕ	$1/\phi$	$10^{-6}/H_0$
[Phenylglycine]: 1.85×10^{-3} mol dm ⁻³				
5.01	3.45	0.350	2.86	0.102
5.21	2.98	0.312	3.20	0.162
5.50	2.98	0.245	4.08	0.316
5.85	2.91	0.152	6.58	0.708
6.03	3.45	0.137	7.30	1.071
6.54	3.16	0.058	17.24	3.467
7.00	3.16	0.048	20.83	10.000
7.36	3.16	0.038	26.32	22.909

Table 4. Effect of Thionine Concentration on ϕ .

[N-Phenylglycine] = 13.85×10^{-4} mol dm ⁻³		Buffer: Acetate
Solvent: absolute methanol		Temperature: $25 \pm 0.1^\circ\text{C}$
10^6 [thionine] (mol dm ⁻³)	$10^{10}I_0$ (E/s)	Quantum efficiency (ϕ)
1.0	2.98	0.148
2.0	2.91	0.143
4.0	2.87	0.137
6.0	3.35	0.165
8.0	2.87	0.137

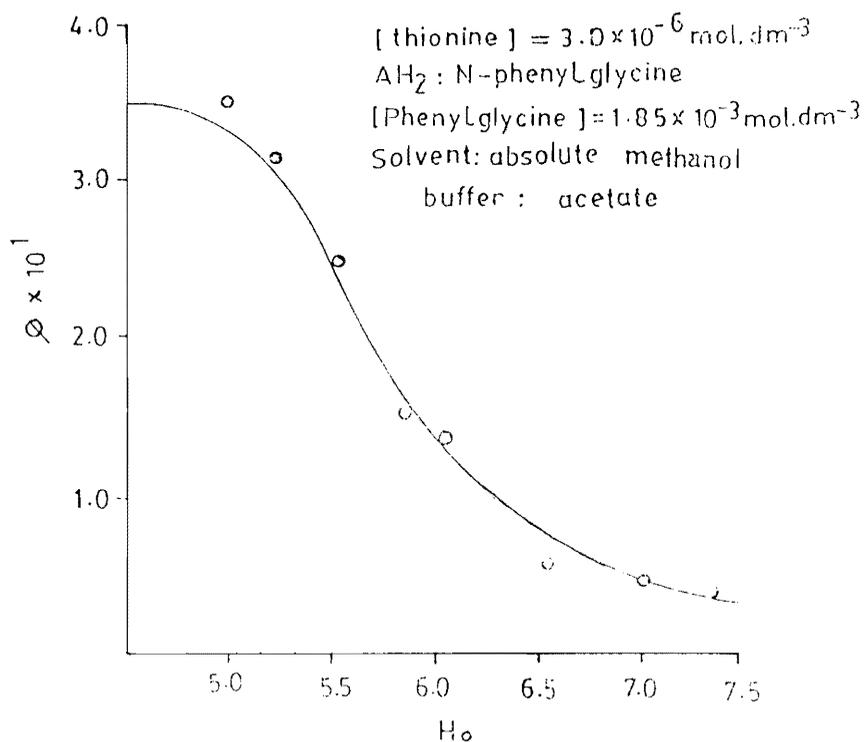


Figure 5. Effect of Acidity on Quantum Efficiency.

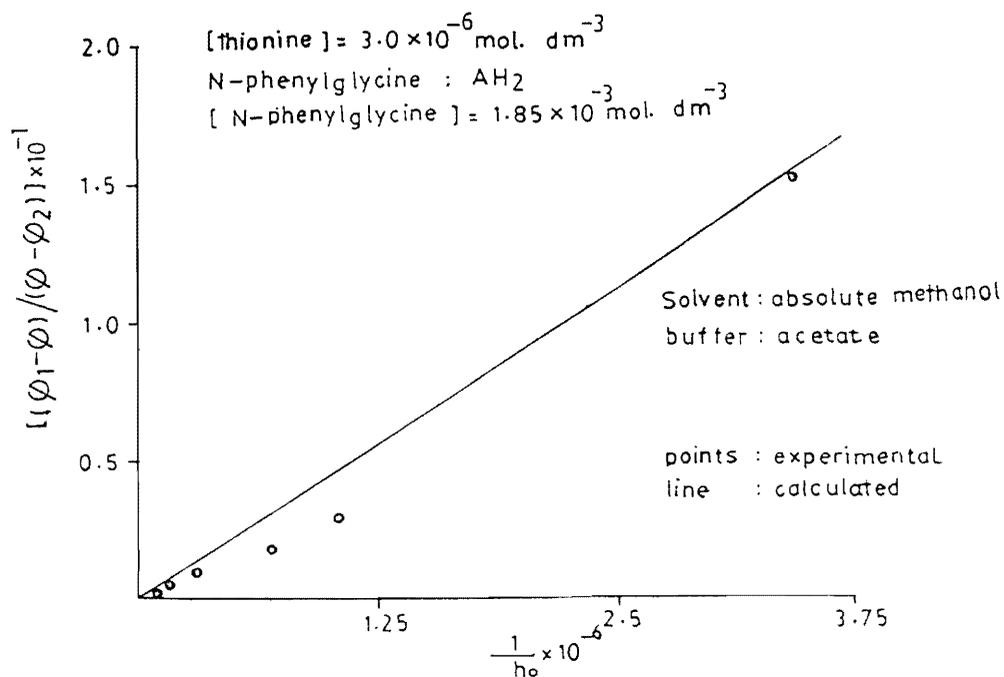


Figure 6. Plot of $(\phi_1 - \phi) / (\phi - \phi_2)$ Against $1/h_o$.

The straight line plots of $1/\phi$ against $1/[AH_2]$ shown in Figure 3 indicate that both the intercepts and slopes are the functions of acidity. The intercepts provide limiting values of ϕ for an infinite concentration of *N*-phenylglycine at two different values of acidity.

In view of the above assumptions, the general mechanism is proposed as follows:



On absorption of light, the cation of thionine excited to a singlet state ThH_s^+ , from which it returns to the ground state by emitting fluorescence:



On the basis of the evidence provided by Pestemer [26], that the fluorescence of thionine is not quenched when photochemical reaction with the substance is taking place, it will be assumed that the reacting excited state is the triplet state. Hence the reaction,



must be included.

In the singlet state the excited thionine may be deactivated to the cation ThH^+ , by collision with unexcited thionine or with reductant:



It is proposed that the dye in triplet state quickly associates with a hydrogen ion, establishing the equilibrium:



$$k_1 = \frac{[{}^3ThH_2^{++}]}{[{}^1ThH^+][H^+]} . \quad (12)$$

In the triplet state the excited thionine may be deactivated to the cation ThH^+ , by collision with reductant molecule:



The triplet state is supposed to react with reductant forming semithionine:



In the triple state the excited thionine may form cation ThH^+ by intersystem crossing:



The protonated triplet species are supposed to react with the reductant forming semithionine which on disproportionation produces the leucothionine:

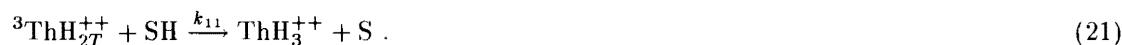


Assuming that the ${}^3\text{ThH}_2^{++}$ associates with AH_2 , the equilibrium is established:

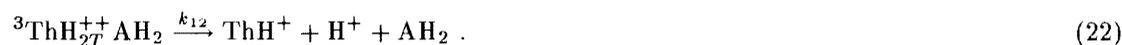


$$k_2 = \frac{[{}^3\text{ThH}_{2T}^{++} \text{AH}_2]}{[{}^3\text{ThH}_2^{++}] [\text{AH}_2]} . \quad (20)$$

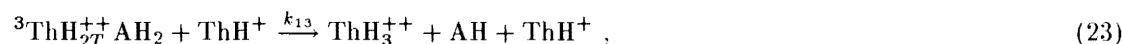
Reaction with the solvent (SH) is:



By the internal conversion the complex loses its energy and subsequently dissociates:



In the presence of unexcited thionine the oxidation-reduction reaction occurs between the two parts of the complex apparently:



where AH is the free radical from AH_2 and ThH_3^{++} is semithionine. This is a hydrogen transfer reaction.

By the transfer of the electron, the oxidation reduction reaction can also take place:



ThH_3^{++} disproportionates to give leucothionine ThH_4^{++} , and thionine cation ThH^+ :



The reactions of the free radical AH cannot be exactly specified but may be written as:



where k_1 to k_{15} represent the rate constants of the respective processes.

Let

$$\begin{aligned} [{}^1\text{ThH}^+] &= a; [{}^3\text{ThH}_2^{++}] = b; [{}^3\text{ThH}_2^{++} \cdot \text{AH}_2] = c; \\ [\text{ThH}^+] &= A; [\text{AH}_2] = l; [\text{H}^+] = h_0 \\ \alpha [I_a] &= (k_5al + k_6al + k_7a) + (k_8bl + k_9bl + k_{10}b + k_{11}b) + (k_{12}c + k_{13}cA) \\ &= a(k_5l + k_6l + k_7) + b(k_8l + k_9l + k_{10} + k_{11}) + c(k_{12} + k_{13}A) . \end{aligned} \quad (28)$$

Since

$$\phi = - \frac{d[\text{ThH}^+]}{dt} \Big/ [I_a] , \quad (29)$$

from Equations (12) & (20):

$$\phi = \frac{\alpha(k_6l + k_9h_0lk_1 + k_{11}k_1h_0 + k_{13}k_1k_2h_0lA)}{2(k_5l + k_6l + k_7) + k_1h_0(k_8l + k_9l + k_{10} + k_{11} + k_{12}k_2l + k_{13}Ak_2l)} . \quad (30)$$

Let $\phi = \phi_1$ at high h_0 , and $\phi = \phi_2$ at low h_0 .

At high h_0 , a is negligible, and b and c are the controlling terms, therefore,

$$\phi_1 = \frac{\alpha(k_9l + k_{11} + k_{13}k_2lA)}{2(k_8l + k_9l + k_{10} + k_{11} + k_{12}k_2l + k_{13}k_2Al)} . \quad (31)$$

At low h_0 , the terms b and c are negligible:

$$\phi_2 = \frac{\alpha k_6 l}{2(k_5 l + k_6 l + k_7)} \quad (32)$$

From Equation (30),

$$\frac{(\phi_1 - \phi)}{(\phi - \phi_2)} = \frac{\phi_1}{\phi_2} \times \frac{k_6 l}{(k_9 l + k_{11} + k_{13} k_2 A l) k_1 h_0} \quad (33)$$

The plot of $[(\phi_1 - \phi)/(\phi - \phi_2)]$ against $1/h_0$ is a straight line passing through the origin.

From Equation (30)

If $\phi_2 = 0$, i.e. $k_6 = 0$; therefore:

$$\frac{1}{\phi} = \frac{2}{\alpha} + \frac{2(k_8 l + k_{10} + k_{12} k_2 l)}{\alpha(k_9 l + k_{11} + k_{13} k_2 A l)} + \frac{2(k_5 l + k_7)}{\alpha(k_9 l + k_{11} + k_{13} k_2 A l) h_0 k_1} \quad (34)$$

k_{11} can be neglected towards high l , and Equation (34) could be written as:

$$\frac{1}{\phi} = \frac{2(k_5 l + k_6 l + k_7) + k_1 h_0 (k_8 l + k_9 l + k_{10}) + k_2 k_1 h_0 l}{\alpha(k_6 l + k_9 l h_0 k_1 + k_{13} k_1 k_2 h_0 A l)} (k_{12} + k_{13} A) \quad (35)$$

Thus the intercept of $1/\phi$ against $1/l$ is,

$$\frac{1}{\phi_\infty} = \frac{2}{\alpha} \frac{(k_5 + k_6 + k_8 h_0 k_1 + k_9 h_0 k_1) + (k_{12} + k_{13} A) h_0 k_1 k_2}{(k_6 + k_9 h_0 k_1 + k_{13} k_2 k_1 A h_0)} \quad (36)$$

and the slope is:

$$\frac{(k_7 + k_{10} k_1 h_0)}{(k_6 + k_9 h_0 k_1 + k_{13} k_2 k_1 A h_0)} \quad (37)$$

At infinite concentration of the reductant, the intercept $1/\phi_\infty$ gives the limiting quantum efficiency. Thus the plot of $1/\phi$ against $1/l$ can also be written as:

$$\frac{1}{\phi} = \frac{1}{\phi_\infty} + \frac{2}{\alpha} \frac{(k_7 + k_{10} k_1 h_0)}{k_6 + k_9 h_0 k_1 + k_{13} k_1 k_2 A h_0} \frac{1}{l} \quad (38)$$

The values of the intercepts and slopes of the plots of reciprocal of the quantum efficiency ($1/\phi$) against the reciprocal of the reductant concentration ($1/[AH_2]$) as shown in Figure 4 were calculated. These values are as follows:

<i>N</i> -Phenylglycine	H_0	Intercept	10^3 Slope (mol dm ⁻³)
	5.57	2.97 ± 0.22	3.58 ± 0.80
	5.90	1.58 ± 0.14	3.13 ± 0.52

The ratios of the rate constants were calculated using the different equations of the general mechanism. For instance, the ratios:

$$\frac{2}{\alpha} \times \frac{(k_5 + k_6)}{k_6}, \quad \text{and} \quad \frac{2}{\alpha} \times \frac{(k_8 + k_9)}{k_9 + k_{13}k_2A}$$

were calculated from

$$\phi_2 = \frac{\alpha k_6 l}{2(k_5 l + k_6 l)} \quad (k_7 \text{ is neglected}),$$

and

$$\phi_1 = \frac{\alpha(k_9 l + k_{13}k_2Al)}{2(k_8 l + k_9 l)} \quad (k_{10} - k_{13} \text{ in the denominator are neglected}).$$

Using the slopes of the plots of $1/\phi$ against $1/[AH_2]$ *i.e.* $1/l$, the ratios of the rate constants

$$\frac{2}{\alpha} \left(\frac{k_7}{k_6} \right) \quad \text{and} \quad \frac{2}{\alpha} \times \frac{k_{10}}{(k_9 + k_{13}k_2A)}$$

were calculated.

The ratios of the rate constants $k_6/[(k_9 + k_{13}k_2A)k_1]$ were calculated from the plots of $(\phi_1 - \phi)/(\phi - \phi_2)$ against $1/h_0$. The value

$$\frac{2}{\alpha} \times \frac{(k_{12} + k_{13}A)k_2}{(k_9 + k_{13}k_2A)k_1}$$

was determined from the intercept of the plot of $1/\phi$ against $1/[AH_2]$ *i.e.* $(1/l)$. The values of the ratios of the rate constants for the reactions of thionine with *N*-phenylglycine in absolute methanol are summarized in Table 5.

$(2/\alpha)[(k_5 + k_6)/k_6]$ is concerned with the ${}^1\text{ThH}_T^+$ species. At the comparative high acidity region the quantum efficiency is due to k_6 . The rate constant k_6 as compared to k_5 is low with *N*-phenylglycine in absolute methanol.

k_8 and k_9 are due to ThH_2T^{++} in the comparative low acidity region. The rate constant k_8 and k_9 are responsible to advance the chemical reaction.

$k_6/[(k_9 + k_{13}k_2A)k_1]$ is the ratio of the rate constants responsible for producing products by three species *i.e.*, triplet state of thionine, protonated triplet state thionine and association of protonated triplet state of

thionine with reductant. $(2/\alpha)/(k_7/k_6)$ is the ratio of the rate constant between intersystem crossing rate and the products forming rate for species ThH_T^+ .

$(2/\alpha)/[k_{10}/(k_9 + k_{13}k_2A)]$ is the ratio of the rate constant between internal conversion rate of ThH_{2T}^{++} and the products forming rate due to the species ThH_{2T}^{++} and $\text{ThH}_{2T}^{++} \cdot \text{AH}_2$. $(\alpha/2)[k_6/(k_{10}k_1)]$ is the ratio of the rate constant responsible for producing products by the species ThH_T^+ and internal conversion process of ThH_{2T}^{++} . $(2/\alpha)\{k_7/[(k_9 + k_{13}k_2A)k_1]\}$ is the ratio of the rate constant between intersystem crossing of the process ThH_T^+ and the rate of the formation of the products by ThH_{2T}^{++} and association. k_{12} and k_{13} are due to the dissociation of the complex ($\text{ThH}_{2T}^{++} \cdot \text{AH}_2$) and the products formed by the thionine cation with association. k_9 is due to the combination of reductant with the protonated state of thionine. The ratio $[(k_{12} + k_{13}A)k_2]/[(k_9 + k_{13}k_2A)k_1]$ indicates that the mechanism of the reactions of thionine with reductant (*N*-phenylglycine) also involves association. Various equations were derived from the postulated mechanism. The Equations [33], [34], and [38] show the relations between $1/\phi$ versus $1/[\text{AH}_2]$ and $(\phi_1 - \phi)/(\phi - \phi_2)$ versus $1/h_0$. The plots of $1/\phi$ versus $1/[\text{AH}_2]$, $(\phi_1 - \phi)/(\phi - \phi_2)$ versus $1/h_0$ drawn from experimental data leads to the conclusions that there exists linear relations, which is in accordance with the equations derived from the proposed mechanism.

Table 5. Ratios of the Rate Constants.

(1)	$\frac{2}{\alpha} \times \frac{(k_5 + k_6)}{k_6}$	26.32
(2)	$\frac{2}{\alpha} \times \frac{(k_8 + k_9)}{(k_9 + k_{13}k_2A)}$	2.86
(3)	$\frac{10^5 \times k_6}{(k_9 + k_{13}k_2A)k_1}$	4.83 ± 1.24
(4)	$\frac{2}{\alpha} \times \frac{10^3 \times k_{10}}{(k_9 + k_{13}k_2A)}$	3.58 ± 0.80
(5)	$\frac{2}{\alpha} \times \frac{10^3 \times k_5}{(k_9 + k_{13}k_2A)k_1}$	1.30 ± 0.30
(6)	$\frac{2}{\alpha} \times \frac{10^8 \times k_7}{(k_9 + k_{13}k_2A)k_1}$	16.15 ± 6.0
(7)	$\frac{2}{\alpha} \times \frac{10^3 \times k_7}{k_6}$	3.13 ± 0.52
(8)	$\frac{2}{\alpha} \times \frac{(k_{12} + k_{13}A)k_2}{(k_9 + k_{13}k_2A)k_1}$	0.10 ± 0.22
(9)	$\frac{\alpha}{2} \times \frac{10^2 \times k_6}{(k_{10} \times k_1)}$	1.34 ± 0.08

ACKNOWLEDGEMENTS

I am grateful to Professor Dr. M. Ghaziuddin Ahmed for valuable suggestions and Mr. M. Ayub Khan Yousufzai, Department of Applied Physics for technical help.

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Paper Received 10 October 1993; Revised 19 October 1994; Accepted 8 January 1995.